



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : <b>C09K 21/14, 3/10, C08K 13/06 C08L 75/04</b>		A1	(11) International Publication Number: <b>WO 94/06886</b> (43) International Publication Date: <b>31 March 1994 (31.03.94)</b>
<p>(21) International Application Number: <b>PCT/EP93/02494</b></p> <p>(22) International Filing Date: <b>15 September 1993 (15.09.93)</b></p> <p>(30) Priority data: <b>P 42 31 342.2 18 September 1992 (18.09.92) DE</b></p> <p>(71) Applicant (for AU only): <b>BOSTIK AUSTRALIA PTY. LTD [AU/AU]; 51 High Street, Thomastown, VIC 3074 (AU).</b></p> <p>(71) Applicant (for ES FR only): <b>BOSTIK S.A. [FR/FR]; 19, route Nationale, F-77170 Coubert (FR).</b></p> <p>(71) Applicant (for GB only): <b>BOSTIK LIMITED [GB/GB]; Ulverscroft Works, Ulverscroft Road, Leicester LE4 6BW (GB).</b></p>		<p>(71) Applicant (for JP KR only): <b>BOSTIK INC. [US/US]; c/o The Corporate Trust Company, Corporate Trust Center, 1209 Orange Street, Wilmington, DE 19801 (US).</b></p> <p>(71) Applicant (for SE only): <b>BOSTIK AB [SE/SE]; Strandbads-vægen, S-252 29 Helsingborg (SE).</b></p> <p>(72) Inventor; and</p> <p>(75) Inventor/Applicant (for US only) : <b>JOACHIMI, Roland [DE/DE]; Wolfsweg 9, D-7120 Bietigheim-Bissingen (DE).</b></p> <p>(74) Agent: <b>DUBOST, Thierry; Cray Valley S.A., Service Propriété Industrielle, BP 22, F-60550 Verneuil-en-Halatte (FR).</b></p> <p>(81) Designated States: <b>AU, JP, KR, US, European patent (ES, FR, GB, SE).</b></p> <p><b>Published</b> <i>With international search report.</i></p>	
<p>(54) Title: <b>INTUMESCENT ONE-COMPONENT SEALANT</b></p> <p>(57) Abstract</p> <p>The invention relates to an intumescent one-component sealant based on polyurethane and containing an intumescent agent and a vitreous fusible filler. The intumescent agent and the vitreous filler have been pretreated by reaction with an isocyanate having a functionality of at least 2. The sealant is stable in storage and is an effective fire barrier in the event of fire.</p>			
<p><b>BEST AVAILABLE COPY</b></p>			

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NE	Niger
BE	Belgium	GN	Guinea	NL	Netherlands
BF	Burkina Faso	GR	Greece	NO	Norway
BG	Bulgaria	HU	Hungary	NZ	New Zealand
BJ	Benin	IE	Ireland	PL	Poland
BR	Brazil	IT	Italy	PT	Portugal
BY	Belarus	JP	Japan	RO	Romania
CA	Canada	KP	Democratic People's Republic of Korea	RU	Russian Federation
CF	Central African Republic	KR	Republic of Korea	SD	Sudan
CG	Congo	KZ	Kazakhstan	SE	Sweden
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovak Republic
CM	Cameroon	LU	Luxembourg	SN	Senegal
CN	China	LV	Latvia	TD	Chad
CS	Czechoslovakia	MC	Monaco	TG	Togo
CZ	Czech Republic	MG	Madagascar	UA	Ukraine
DE	Germany	ML	Mali	US	United States of America
DK	Denmark	MN	Mongolia	UZ	Uzbekistan
ES	Spain			VN	Viet Nam
FI	Finland				

**INTUMESCENT ONE-COMPONENT SEALANT.**

The invention relates to an intumescent one-component sealant comprising a polyurethane binder, an intumescent agent and, if required, conventional additives, to a process for preparing such a 5 sealant, and to the use thereof for sealing openings or joints in construction parts.

One- and two-component sealants based on polyurethane are often used as high-performance sealing materials in the construction industry, for example for the elastic sealing of settlement joints 10 between prefabricated concrete elements. In the event of fire, the sealing material is generally not capable of preventing, as fire barrier, passage of the flames through the joint for more than 20 minutes. Specially formulated sealants are therefore necessary to keep the joints closed for hours even in the event of fire.

15 It is already known, namely by EP-A-420302, that a composition of a polyurethane binder, an intumescent substance and glass frits as glass-like melting filler provides an intumescent material ; this document however does not provide an indication about a preparation of the glass-like filler by means of an isocyanate.

20 In DE-A-3421086 it is described the reaction of an aqueous alkaline silicate solution with a polyisocyanate and a polyol. The reaction product however is a tridimensional crosslinked organomineral without the property of intumescence.

From DE-A-1118966 it is known a flame-resistant sealant 25 composition which comprises a crosslinked polyurethane and a silicic acid filler which before crosslinking of the binder was dissolved, at least in colloidal state, in a fluid adduct of a component comprising OH- groups and an isocyanate. This composition however is not intumescent and the silicic acid was not prepared with an 30 isocyanate alone.

JP-A-52/102395 describes a fire-resistant sealing composition made from a foamable polyurethane and an aqueous sodium silicate solution. However in this document can be found no mention of the 35 addition of a glass-like melting filler prepared from an isocyanate to intumescent polyurethane sealing composition.

The purpose of the present invention is to provide intumescent one-component sealants which are in particular stable on storage and are an effective fire barrier in openings and joints of construction parts in the event of fire. A second objective of the 5 present invention is to indicate a process for preparing a sealant of this kind.

The present invention therefore relates to an intumescent one-component sealant comprising a polyurethane binder and an intumescent agent and, if required, conventional additives, 10 characterised in that it further contains a vitreous fusible filler and in that the intumescent agent and the vitreous filler have been subjected to a pretreatment by reaction with an isocyanate having a functionality of at least 2.

The polyurethane binder used in the sealant according to the 15 invention is, for example, a polyurethane prepolymer. The starting components for preparing such polyurethane prepolymers, such as polyols, isocyanates and catalysts, are very well known in polyurethane chemistry.

The sealants according to the invention are moisture-curing. 20 In order to prevent premature curing before application, the sealants are therefore stored in impermeable containers, for example in aluminium or plastics cartridges, with the exclusion of moisture.

The vitreous filler used according to the invention preferably 25 has a wide melting range of approximately 300 to 900°C and serves to improve the properties of the sealant as a fire barrier in the event of fire. Glass frit materials are especially suitable for this purpose, a glass frit material having a melting range of about 350 to 700°C being especially preferred. Such vitreous fillers having a wide melting 30 range are available commercially, for example under the tradename "Ceepree" for a glass frit material having a melting range of 350-700°C, which devitrifies above 800°C and forms a fireproof barrier layer.

Suitable intumescent agents are the substances conventionally 35 used, for example, ammonium polyphosphate, expandable graphite, dicyandiamide, melamine and its derivatives, such as melamine

phosphate, melamine resins or melamine cyanurate, guanidine salts and cyanuric acid derivatives. Especially advantageous results are obtained with ammonium polyphosphates. These are compounds of the general formula  $(\text{NH}_4\text{PO}_3)_n$  where  $n = 20-1000$  and molecular weights of approximately 2000 to 100,000. Such compounds are also available commercially, for example under the name Phos-cheek.

5 The intumescent agents are suitably used in a quantity of approximately 2 to 10 % by weight and the vitreous filler in a quantity of approximately 5 to 15 % by weight, in each case based on 10 the total weight of the sealant.

Surprisingly, it is possible according to the present invention to obtain a storage-stable one-component sealant based on polyurethane if the intumescent agent and the vitreous fusible filler are subjected to a pretreatment by reaction with an isocyanate 15 having a functionality of at least 2 before being mixed with the polyurethane binder. It is assumed that the reactive surfaces of the intumescent agent and the filler are blocked or deactivated by this pretreatment. The term "isocyanate having a functionality of at least 2" here is taken to mean isocyanates having 2 or more isocyanate 20 groups per molecule. Suitable isocyanates for this reaction are conventional diisocyanates and low molecular-weight polyisocyanates, aromatic diisocyanates such as diphenylmethane 4,4'-diisocyanate (MDI), toluylene diisocyanate (TDI) and derivatives thereof being especially preferred.

25 The invention likewise relates to a process for preparing a one-component sealant of this type, which is characterised in that an intumescent agent and a vitreous fusible filler are reacted with an isocyanate having a functionality of at least 2 and the components thus pretreated are mixed with a polyurethane binder and, if 30 required, conventional additives.

Conventional additives which can be added to the sealant according to the invention are, for example, thickening agents, such as bentonite or silicic acid, pigments, such as titanium dioxide, flame retardants, such as antimony trioxide, fillers such as chalk or 35 silicates and the like.

The one-component sealant according to the invention is a very effective fire barrier in openings and joints in construction parts. Furthermore it has the advantages of a moisture-curing one-component sealant, such as simple application, outstanding mechanical properties, such as low modulus, high extensibility and elastic recovery, good adhesion to many substrates and good weather resistance.

The invention is explained in greater detail in the following examples, where all parts are indicated by weight.

## 10 Comparative Example 1

The following basic formulation is used :

1.	Titanium dioxide	8.0
2.	Diisodecyl phthalate	21.0
3.	Chalk (ground ; dried for 24 hours at 130°C)	30.0
15	4. PVC powder/emulsion polymer	10.0
5.	Prepolymer (45.73 % polyether diol* and 43.45 % polyether triol** 10.8 % TDI, free NCO = 440 mVal/kg)	30.0
20	6. Tosyl isocyanate	0.5
7.	Adhesion promoter (Union Carbide Silane A 187)	0.4
8.	Dibutyltin dilaurate	0.1
* Molecular weight approximately 2000, based on polypropylene glycol.		
25	** Molecular weight approximately 4000, based on polypropylene glycol.	

Components Nos. 1 to 5 are homogeneously mixed with stripper in a vacuum dissolver, then component No. 6 is added and mixed for a further 15 minutes. Finally components Nos. 7 and 8 are added and the mixture is mixed under vacuum for 10 minutes and degassed.

### Comparative Example 2

Components Nos. 1 to 5 from Comparative Example 1 are mixed together with 5.0 parts of ammonium polyphosphate, the rest of the procedure being as in Comparative Example 1.

Comparative Example 3

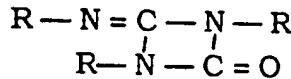
To components Nos. 1 to 5 from Comparative Example 1 are added 5.0 parts of ammonium polyphosphate and 10.0 parts of a commercial glass frit material (melting range 350-700°C, dried for 5 24 hours at 130°C), the rest of the procedure being as in Comparative Example 1.

Example 1

To components Nos. 1 and 2 from Comparative Example 1 are added :

10 5.0 parts of ammonium polyphosphate,  
10.0 parts of a commercial glass frit material  
(melting range 350-700°C, dried for 24 hours at 130°C),  
1.0 part of a commercial aromatic diisocyanate\*  
0.02 part of dibutyltin dilaurate

15 (\* an 80:20 mixture of MDI and the uretonimine derivative of MDI,  
i.e. the cyclo adduct of MDI to the carbodiimide of the MDI



where R = C<sub>6</sub>H<sub>4</sub> - CH<sub>2</sub> - C<sub>6</sub>H<sub>4</sub>NCO).

20 Mixing is continued slowly for one hour at 60 to 70°C in order to complete the reaction. After cooling to 45°C components Nos. 3 to 5 according to Comparative Example 1 are added, the rest of the procedure being as in comparative Example 1.

Example 2

25 To components Nos. 1 and 2 from Comparative Example 1 are added :

3.0 parts of ammonium polyphosphate  
10.0 parts of a commercial glass frit material  
(melting range 350-700°C, dried for 24 hours at 130°C),  
30 0.8 part of MDI (flakes)  
0.02 part of dibutyltin dilaurate.

The rest of the procedure is as in Example 1.

Example 3

To components Nos. 1 and 2 from Comparative Example 1 are 35 added

5.0 parts of melamine cyanurate

10.0 parts of a commercial glass frit material  
(melting range 350-700°C, dried for 24 hours at 130°C),  
1.0 part of a commercial aromatic diisocyanate (as in Example 1)  
0.02 part of dibutyltin dilaurate.  
5 The rest of the procedure is as in Example 1.

Testing the effectiveness as a fire barrier:

Test specimens (12 x 12 x 15 mm, between concrete) are prepared from the sealants according to Comparative Examples 1 to 3 and Examples 1 to 3 and stored at room temperature for 4 weeks.

10 A Simmon-Müller furnace is heated to  $\geq 1000^{\circ}\text{C}$ . The cover of the furnace has a gap of approximately 12 x 50 mm. In each case one test specimen is fixed over this gap so that the sealant closes the gap (test joint). The time for which the gap remains closed, that is to say until the sealant "burns through", is recorded. The results are shown

15 in the table below.

Testing the storage stability:

The sealants prepared according to Comparative Examples 1 to 3 and Examples 1 to 3 are filled into cartridges. The viscosity is determined 4 hours after preparation ( $\eta_1$ ).

20 One further cartridge in each case is stored for 4 weeks at 40°C. After this time the viscosity of the stored specimen is determined again. The ratio  $\eta_2/\eta_1$  serves as a measure of the storage stability. The results are also shown in the table below.

Table

Example	Compa			Compa		
	1	2	3	1	2	3
Fire barrier (time until failure)						
	20 min	40 min.	> 2 h	> 2 h	> 2 h	> 2 h
Storage stability ( $\eta_2/\eta_1$ )	1.5	gelled	gelled	1.8	1.7	2.0

CLAIMS

1. Intumescent one-component sealant comprising a polyurethane binder and an intumescent agent and, if required, conventional additives, characterised in that it further contains a vitreous fusible filler and in that the intumescent agent and the vitreous filler have been subjected to a pretreatment by reaction with an isocyanate having a functionality of at least 2.
- 5 2. Sealant according to Claim 1, characterised in that it contains an ammonium polyphosphate as intumescent agent.
- 10 3. Sealant according to Claim 1 or 2, characterised in that the vitreous filler has a melting range of 300 to 900°C.
4. Sealant according to Claim 3, characterised in that the vitreous filler is a glass frit material.
- 15 5. Sealant according to one of claims 1 to 4, characterised in that the intumescent agent is present in a quantity of 2 to 10 % by weight, based on the total weight of the sealant.
6. Sealant according to one of claims 1 to 5, characterised in that the vitreous filler is present in a quantity of 5 to 15 % by weight, based on the total weight of the sealant.
- 20 7. Sealant according to one of claims 1 to 6, characterised in that the isocyanate is chosen from aromatic isocyanates.
8. Sealant according to Claim 7, characterised in that the aromatic isocyanate is chosen from diphenylmethane 4,4'-diisocyanate, toluylene diisocyanate and derivatives thereof.
- 25 9. Process for preparing an intumescent one-component sealant according to Claim 1, characterised in that an intumescent agent and a vitreous fusible filler are reacted with an isocyanate having a functionality of at least 2 and the components thus pretreated are mixed with a polyurethane binder and, if required, conventional additives.
- 30 10. Use of a one-component sealant according to one of Claims 1 to 8 for the effective sealing, in the event of fire, of openings and joints in construction parts.

## INTERNATIONAL SEARCH REPORT

Int'l Application No  
PCT/EP 93/02494A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 C09K21/14 C09K3/10 C08K13/06 C08L75/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 5 C09K C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 175 447 (TEXACO DEVELOPEMENT CORPORATION) 26 March 1986 see page 2, line 35 - page 3, line 3 see page 6, line 7 - page 7, line 23 see page 9, line 7 - line 15; claims 1,3,10 ---	1,7,8
A	EP,A,0 420 302 (CROMPTON) 3 April 1991 cited in the application see the whole document ---	1-4,10
A	DATABASE WPI Week 9144, Derwent Publications Ltd., London, GB; AN 91-320279 & JP,A,3 212 479 (MITSUBISHI CABLE IND.) 18 September 1991 see abstract ---	1,3,4,10
-/-		

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*'A' document defining the general state of the art which is not considered to be of particular relevance
- \*'B' earlier document but published on or after the international filing date
- \*'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*'O' document referring to an oral disclosure, use, exhibition or other means
- \*'P' document published prior to the international filing date but later than the priority date claimed

- \*'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*'Z' document member of the same patent family

Date of the actual completion of the international search  20 December 1993	Date of mailing of the international search report  23.12.93
Name and mailing address of the ISA  European Patent Office, P.B. 5818 Patentiaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Authorized officer  Puettz, C

## INTERNATIONAL SEARCH REPORT

Inten  
nal Application No  
PCT/EP 93/02494

## C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 097 400 (J. WORTMANN, F.-J. DANY, J. KANDLER) 27 June 1978 see the whole document ----	1,2
A	DE,A,38 13 251 (LENTIA GMBH) 9 November 1989 see the whole document ----	1
A	GB,A,2 115 739 (GENERAL MOTORS CORPORATION) 14 September 1983 see the whole document ----	1
A	DE,A,34 21 086 (KVT KUNSTSTOFFVERFAHRENSTECHNIK) 12 December 1985 cited in the application see the whole document -----	1,9
A	DE,A,11 18 966 (IMPERIAL CHEMICAL INDUSTRIES) 28 January 1960 cited in the application -----	1

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

Intern.	nal Application No
PCT/EP 93/02494	

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0175447	26-03-86	CA-A-	1273448	28-08-90
		JP-C-	1637309	31-01-92
		JP-B-	3002445	16-01-91
		JP-A-	61064712	03-04-86
		US-A-	4607090	19-08-86
EP-A-0420302	03-04-91	AU-B-	610867	30-05-91
		AU-A-	1448588	13-10-88
		DE-A-	3882070	05-08-93
		EP-A, B	0287293	19-10-88
		GB-A-	2203157	12-10-88
		GB-A-	2234754	13-02-91
		JP-A-	63273690	10-11-88
		US-A-	4879066	07-11-89
US-A-4097400	27-06-78	DE-A-	2359700	05-06-75
		AT-B-	337997	25-07-77
		BE-A-	822756	29-05-75
		CA-A-	1050698	13-03-79
		CH-A-	603730	31-08-78
		FR-A, B	2253063	27-06-75
		GB-A-	1473598	18-05-77
		NL-A-	7415621	03-06-75
		SE-B-	415774	27-10-80
		SE-A-	7414962	02-06-75
DE-A-3813251	09-11-89	NONE		
GB-A-2115739	14-09-83	CA-A-	1190713	23-07-85
		DE-A, C	3307160	15-09-83
		US-A-	4564491	14-01-86
DE-A-3421086	12-12-85	EP-A, B	0167002	08-01-86
		JP-C-	1758403	20-05-93
		JP-B-	4041690	09-07-92
		JP-A-	61002721	08-01-86
		US-A-	4871829	03-10-89
		US-A-	4827005	02-05-89
DE-A-1118966		NONE		

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**